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NASA TM-77615

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N84-34709

G3/35 Unclass
24063



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546
OCTOBER 1984

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STANDARD TITLE PAGE

1. Report No. NASA TM-77619	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle MAGNETIC RECORD SUPPORT		5. Report Date October 1984	
		6. Performing Organization Code	
7. Author(s) Nakayama, M., Morita, H., Tokukawa, Y., Izumi, T., Fukuda, K., Kubota, Y.		8. Performing Organization Report No.	
		10. Work Unit No.	
9. Performing Organization Name and Address Leo Kanner Associates, Redwood City, California 94603		11. Contract or Grant No. NASW-3541	
		13. Type of Report and Period Covered Translation	
12. Sponsoring Agency Name and Address National Aeronautics and Space Admin- istration, Washington D.C., 20546		14. Sponsoring Agency Code	
15. Supplementary Notes Translation of "Magnetischer Aufzeichnungsträger," German Patent No. DE 3321907 A1, December 22, 1983, pp. 1-23			
16. Abstract <p>The magnetic layer of a magnetic record support is coated with a thin film of a polymer with a siloxane bond. The magnetic layer consists of a thin film obtained by vacuum metallization, cathode sputtering or dispersion of a ferromagnetic metal powder in a binder. The polymer with a siloxane bond is produced by the polymerization of an organic silicon compound which inherently contains or is able to form this bond. Polymerization is preferably performed by plasma polymerization.</p>			
17. Key Words (Selected by Author(s))		18. Distribution Statement Unclassified-unlimited	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 19	22.

MAGNETIC RECORD SUPPORT

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Claims

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1. Magnetic record support with a film base and a magnetic layer formed on it, characterized in that the magnetic layer is covered by a thin film made of a polymer with a siloxane bond.

2. Magnetic record support as in Claim 1, characterized in that the magnetic layer consists of a thin film formed by vacuum metallization, cathode sputtering or dispersion of a ferromagnetic metal powder in a binder.

3. Magnetic record support as in Claim 1 or 2, characterized in that the polymer with a siloxane bond is produced by the polymerization of an organic silicon compound which inherently contains or is able to form this bond.

4. Magnetic record support as in Claim 1, characterized in that the polymerization is performed in a plasma polymerization process.

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[Description]

The invention concerns a magnetic record support with a film base and a magnetic layer formed on it.

A considerable time has passed since the first introduction of magnetic record supports consisting of a non-magnetic film base and a magnetic layer formed on it, particularly consisting

*Numbers in the margin indicate pagination in the foreign text.

of a binder and a magnetic powder of an oxide such as $\gamma\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_3\text{O}_4$ or Co-doped $\gamma\text{-Fe}_2\text{O}_3$. Subsequently, record supports for recordings with higher densities were developed, with a coating consisting of a binder and a ferromagnetic powder such as Fe, Co, Ni, Fe-Co, Co-Ni, Fe-Co-Ni, Fe-Co-B, Fe-Co-Cr-B, Mn-Bi, Mn-Al or Fe-Co-V. Most recently, increasing attention has been given to record supports presenting a magnetic coating made of vacuum-evaporated metal or a film obtained by cathode sputtering.

Magnetic record supports, particularly for use as magnetic /3 tapes and disks, must have a low coefficient of friction, be able to run uniformly and stably, be wear-resistant, present stable operating performance over extended durations of use, undergo little or no change in their properties, ensure reproducible characteristics at all times under prescribed ambient conditions, be durable and present a long lifespan.

In addition to these requirements, the surface smoothing of magnetic record supports has been examined, where a ferromagnetic layer is provided for high-density recordings or where supports are equipped with a film formed by vacuum metallization or cathode sputtering. Because of a tendency to higher coefficients of friction, countermeasures must be taken to guarantee a uniform, stable running of the record supports. A further problem with such record supports is the possibility of degeneration because of the corrosion of free metal particles in the coatings. Consequently there is a particularly strong need for magnetic record supports with higher running stability, smoothness and durability than before, so that the information recorded at high density can be stored long-term and can be reproduced reliably and faithfully at any time.

In such record supports, usually silicon oil or another lubricant is used, which is either mixed with the magnetic coating material by kneading or applied on top of the magnetic layer. /4

The magnetic layer has also already been provided with a covering layer in the form of a specially formed thin film. The conventional measures, however, have proved to be unsatisfactory because the lubricants are hard to mix with the magnetic coating material or are hard to apply uniformly to the magnetic coatings, and because the lubrication and other achieved effects are only short-lived and decline with use. Increased thickness of the film leads, moreover, to a drop in output because of spacing losses. Hence the formation of a thin, durable coating capable of achieving the desired effects has proved to be extremely difficult.

The invention is based on the task of creating a magnetic record support, preferably a record support for the production of high-density recordings, which presents a new kind of thin-film covering layer presenting a combination of low friction, running stability, durability and corrosion resistance, so as to lend the record support improved surface properties.

This task is accomplished under the invention in that the magnetic layer is covered with a thin film of a polymer with a siloxane bond. It developed that such a thin film lends the record support excellent properties. The film can be formed by heat polymerization or the like. The film's properties, however, are even more favorable if the film is precipitated by plasma polymerization on the magnetic layer of a magnetic record support. The plasma polymerization is able to produce a film only 5 to 1000 Å thick, but which still provides a protective effect and produces the aforementioned improvements of the surface properties of the record support. In this way, any output drop of the record support that is attributable to spacing losses is ruled out. In practice this is particularly significant, Because plasma polymerization is a gas-phase reaction, the reaction gas easily penetrates into tiny recesses on the surface of the magnetic layer. Testing under an electron microscope shows

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that very small openings on the surface are filled up with the gas. This phenomenon seems to play an important role in the improvement of the record support's corrosion resistance. The plasma polymerization, which allows continuous high-speed formation of a film, can readily be introduced into the production process for the magnetic record support, without any adverse effects on productivity.

The thin film made of a polymer with a siloxane bond improves the surface properties of the record support markedly, without adverse effects on its magnetic or electrical properties or on its ability to produce high-density recordings. This is of outstanding significance in practice.

The invention is explained in more detail below using /6 practical examples. In the attached drawings,

Fig. 1 shows a schematic diagram of a plasma polymerization device with a high-frequency wave discharge, for the formation of a thin film on the magnetic record support under the invention, and

Fig. 2 shows a schematic diagram of a plasma polymerization device with a microwave discharge, intended for the same purpose.

The thin film of a polymer with a siloxane bond can be formed by polymerizing either an organic silicon compound with the siloxane bond, or an organic silicon compound such as a silane which can develop the siloxane bond during polymerization. It has proved to be especially favorable to use a compound able to form a thin film of a polymer that develops the siloxane bond during plasma polymerization. Examples of such substances are:

Tetramethoxysilane, tetraethoxysilane, octamethylcyclotetra-siloxane, hexamethylcyclotetra-siloxane, hexamethoxydisiloxane,

hexaethoxydisiloxane, triethoxyvinyl silane, dimethylethoxyvinyl silane, trimethoxyvinyl silane, methyltrimethoxysilane, dimethoxymethylchlorosilane, dimethoxymethylsilane, trimethoxysilane, 17 dimethylethoxysilane, trimethoxysilanol, hydroxymethyltrimethyl silane, methoxytrimethyl silane, dimethoxydimethyl silane, ethoxytrimethoxysilane, bis(2-chloro-ethoxy)methyl silane, acetoxytrimethyl silane, chloromethyldimethylethoxysilane, 2-chloroethoxytrimethyl silane, ethoxytrimethyl silane, diethoxymethylsilane, ethyltrimethoxysilane, tris(2-chloroethoxy)silane, dimethoxymethyl-3,3,3-trifluoropropyl silane, 1-chloromethyl-2-chloroethoxytrimethyl silane, allyloxytrimethyl silane, ethoxydimethylvinyl silane, isopropenoxytrimethyl silane, 3-chloropropyldimethoxymethyl silane, chloromethyldiethoxymethyl silane, triethoxychlorosilane, 3-chloropropyltrimethoxysilane, diethoxydimethylsilane, dimethoxy-3-mercaptopropylmethyl silane, triethoxysilane, 3-mercaptopropyltrimethoxysilane, 3-aminopropyltrimethoxysilane, diethoxymethylvinyl silane, chloromethyltriethoxysilane, tert.-butoxytrimethyl silane, butyltrimethoxysilane, methyl triethoxysilane, 3-(N-methylaminopropyl)triethoxysilane, diethoxydivinyl silane, diethoxydiethyl silane, ethyltriethoxysilane, 2-mercaptoethyltriethoxysilane, 3-aminopropyldiethoxymethyl silane, p-chlorophenyltriethoxysilane, phenyltrimethoxysilane, 2-cyanoethyltriethoxysilane, allyltriethoxysilane, 3-chloropropyltriethoxysilane, 3-allylaminopropyltrimethoxysilane, propyl triethoxysilane, hexatrimethoxysilane, 3-aminopropyl triethoxysilane, 3-methylacryloxypropyltrimethoxysilane, methyl tris(2-methoxyethoxy)silane, diethoxymethylphenyl silane, p-chlorophenyltriethoxysilane, phenyltriethoxysilane, tetraallyloxysilane, tetrapropoxysilane, tetraisopropoxysilane, dimethoxydiphenyl silane, diethoxydiphenyl silane, tetraphenoxysilane, 1,1,3,3-tetramethyldisiloxane, hexamethyldisiloxane, octamethyltrisiloxane, 1,1,1,-3,5,5,5-heptamethyl trisiloxane, hexaethylcyclotrisiloxane and 1,3,5-trimethyl-1,3,5-triphenyl cyclotrisiloxane.

The plasma polymerization process consists of mixing the /8 discharged plasma of a carrier gas such as Ar, He, H₂ or N₂ with a monomer gas and bringing the mixed gas into contact with the surface of the base, in order to form a plasma-polymerized film on the latter. In principle, an electric field is applied to the gas, which is kept at low pressure, and the free electrons present in small amounts in the gas undergo an acceleration in the electrical field because of the considerable greater intermolecular distance compared to normal pressure. The free electrons assume a kinetic energy (electron temperature) of 5 to 10 eV. If the atoms collide at this speed with other atoms or molecules, they break open the atomic or molecular shell and cause a dissociation into normally unstable chemical components such as electrons, ions and neutral radicals. The dissociated electrons again undergo an acceleration in the electrical field and dissociate in turn other atoms and molecules. Because of this chain-reaction effect, the gas quickly reaches a highly ionized state, or the form known as a plasma gas. If there is little opportunity to collide with electrons, the gas molecules absorb little energy; they are kept at a temperature close to the usual value. The system in which the kinetic energy of the electrons (electron temperature) and the heat movement of the molecules (gas temperature) are separated is called a low-temperature plasma, where the chemical components maintain their original forms, to a large extent, and are ready for an additional chemical reaction such as a polymerization.

In the context of the present invention, the above condi- /9 tions are used to form a plasma-polymerized film over a base. Because of the use of the low-temperature plasma, there are no unfavorable thermal effects on the base.

Figures 1 and 2 show typical devices to form a thin polymer film by plasma polymerization on the surface of a magnetic record support. Figure 1 shows schematically a plasma polymer-

ization device working with a high-frequency discharge, while Fig. 2 shows a plasma polymerization device in which a microwave discharge is used.

Figure 1 shows a polymerization reaction vessel R to which a monomer gas is added from a source 1 and a carrier gas is added from a source 2 via mass flow regulators 3 or 4, after the gases have been mixed by a mixer 5. The monomer gas, i.e., the substance to be polymerized in the reaction vessel, is selected according to this invention from among the organic silicon compounds which have siloxane bonds or can form such bonds during plasma polymerization. Ar, He, H₂, N₂ etc. are usefully employed as the carrier gas. The monomer gas is added at a flowthrough rate in the range of 1 to 100 ml/min, and the carrier gas at a flowthrough rate of 50 to 500 ml/min. Inside the reaction vessel R, there are means to support the magnetic record support to be treated. In the illustrated formula /10 these include a supply roll 9 and a wind-up roll 10 for a magnetic tape. Depending on the form of the record support to be treated, one can work with various other supports, including for example stationary or rotating supports. Two electrodes 7, 7' are arranged horizontally and parallel to each other. The magnetic tape runs between these electrodes. One electrode 7 is connected to a high-frequency energy source 6, while the other electrode 7' is grounded at 8. The vessel R is furthermore equipped with a vacuum system to evacuate the vessel. This system includes a liquid nitrogen trap 11, an oil-sealed rotary pump 12 and a vacuum regulator 13. The vacuum system maintains a vacuum on the order of 0.01 to 10 Torr inside the vessel.

In operation, the reaction vessel R is first evacuated with the oil-sealed rotary pump to a vacuum of greater than 10^{-3} Torr. Then the monomer gas and the carrier gas are added at predetermined flowthrough rates, in a mixed state. The vacuum in the vessel is regulated within a range of 0.01 to 10 Torr.

When the magnetic tape speed and the flowthrough rates of the monomer gas and carrier gas have assumed constant values, the high-frequency energy source is switched on. Then a plasma-polymerized film is precipitated onto the record support as it moves past.

In the plasma polymerization device illustrated in Fig. 2, which works with a microwave discharge. the reaction vessel R is equipped with a discharge plasma chamber 15 which /11 protrudes horizontally from one side of the vessel. At the extreme end of this chamber 15, the carrier gas is fed in from the source 2. The carrier gas introduced into the chamber is ionized to a plasma by the vibrations of a magnetron, and is stabilized as such. The monomer gas is introduced into the reaction vessel via a jet 16 which opens close to the inside end of the plasma chamber 15. With the plasma chamber 15, a support device mounted in the vessel is aligned, consisting in the present practical example of the supply roll 9 and the wind-up roll 10, standing vertically at a distance from one another. The rest of the components correspond to those in Fig. 1.

A d.c. or a.c. discharge can also be used for the plasma source, just like the aforementioned high-frequency or microwave discharge. With a d.c. and a.c. discharge, the plasma copolymerization can be accomplished with an internal electrode process. The thin film of a polymer with a siloxane bond, formed by plasma polymerization on the magnetic layer, ensures low friction, a property attributable to the siloxane bond. Moreover, the three-dimensional polymer structure causes great durability and a particularly secure adhesion to the underlying layer, thus protecting the latter against corrosion.

In the examples below, plasma-polymerized thin films were formed on various samples of magnetic record supports with the polymerization devices shown in Figs. 1 and 2.

Example 1/12

Using a block consisting of 8 parts Co and 2 parts Ni, a 10 μm -thick film base was provided with a 0,1 μm -thick thin film, forming the magnetic layer, in an oblique vacuum metallization process. A plasma-polymerized thin film based on vinyltrimethoxysilane as a monomer gas was precipitated on this magnetic tape. The device illustrated in Fig. 1 was used. The conditions for the plasma polymerization were as follows:

Flowthrough rate of monomer gas	15 ml/min
Carrier gas	argon
Flowthrough rate of carrier gas	50 ml/min
Vacuum	0.5 Torr
High-frequency energy supply	13.56 MHz, 200 W
Magnetic tape speed	30 m/min

Example 2

Using the device in Fig. 2, a polymer film was formed on a magnetic tape by the microwave discharge plasma polymerization of hexamethyl siloxane; the tape had a magnetic layer consisting of a ferromagnetic Fe-Co alloy powder and a binder.

The magnetic tape was produced as follows:

A compound consisting of

Fe-Co metal powder	100 parts
Abrasive (Al_2O_3)	3 parts
Nitrocellulose	6 parts
Epoxy resin (trade name "Epikote 1004")	4 parts
Polyurethane (" " "Nippollan 5033")	10 parts
Solvent	250 parts

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was dispersed for 5 hrs using a sand grinder. After the addition of 4 parts isocyanate ("Coxonate L") the mixture, while being magnetically aligned, was applied to a polyester carrier film 14 μm thick; a magnetic tape was formed in the usual way.

Then the reaction vessel R and the discharge plasma chamber 15 were evacuated with the oil-sealed rotary pump 12, at a pump delivery of 1000 l/min, to a pressure of less than 10^{-3} Torr. Argon, the carrier gas, was added at a flow rate of 100 ml/min. With the vacuum regulator 13 the vacuum in the reaction vessel was kept at 0.5 Torr. An electrical energy of 500 W at a frequency of 2450 MHz was introduced via the magnetron 6; the plasma was stabilized. Then hexamethylsiloxane was fed in through the jet 16 at a flow rate of 25 ml/min. The magnetic tape was rolled from the supply roll 9 onto the wind-up roll 10 at a rate of 3.0 m/min.

Example 3

Under the same conditions as in Example 1, a thin film of a polymer with a siloxane bond was formed on a magnetic tape; /14 however, the magnetic layer was produced at a thickness of 0.1 μm on the 10 μm -thick polyester film by cathode sputtering of a Co-Ni alloy pulver (95% Co, 5% Ni).

The thin films formed as in Examples 1 to 3 were tested for their compositions with a Fourier-transform infrared spectrophotometer (ESCA). It was confirmed that these were films of polymers with siloxane bonds. The film thicknesses were measured by multi-beam interferometry with an ellipsometer. They were 55 \AA for the films in Examples 1 and 3 and 25 \AA for the film in Example 2.

Comparative Experiments on Operating Performance

Samples of the magnetic tapes treated as in Examples 1 to 3 and samples of untreated tapes were tested for the three following factors:

(A) Kinetic Coefficient of Friction, μ_k

The kinetic coefficient of friction μ_k for each sample was determined by the method described in "SHINGAKU GIHO" (Technical Report of the Communications Society), R50-25 (1980). Using this method, the test tape with the magnetic coating pointing inwards was run around a slipring that simulates a conventional magnetic head. On the one end of the tape, a counterweight was suspended, while the other end was attached to a pressure guage. The slipring was rotated and the force of friction of the magnetic tape was determined with the pressure guage. If one labels the force of friction T , the weight of the counterweight W and the angle at which the tape passes around the ring θ , one obtains the coefficient of friction μ_k from the following equation:

$$\mu_k = \frac{1}{\theta} \ln \frac{T}{W}$$

The results of the comparative experiments are summarized below:

	μ_k
Tape from Example 1	0.23
Untreated tape with vacuum-metallized layer	0.60
Tape as in Example 2	0.19
Untreated tape with layer of ferromagnetic alloy powder	0.35
Tape from Example 3	0.22
Untreated tape with layer precipitated by cathode sputtering	0.55

One can recognize from the table that the magnetic record support under the invention has a very low coefficient of friction, and that the tape samples resulted in values for the coefficient of friction that were less than half the values of the untreated tapes.

(B) Standstill Duration

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The tape samples were also tested for their standstill duration properties, or the length of time during which they supplied visible images during reproduction on a videotape recorder.

The results of the comparative experiments were as follows:

	Standstill duration (min)
Tape from Example 1	45
Untreated tape with vacuum-metallized layer	5
Tape as in Example 2	60
Untreated tape with layer of ferromagnetic alloy powder	15
Tape from Example 3	70
Untreated tape with layer precipitated by cathode sputtering	10

The table shows that noteworthy improvements in friction resistance were achieved with the invention.

(C) Resistance to Degeneration Due to Environmental Influences

It is well known that in tapes of the kind described here, oxidation causes deterioration of the magnetic properties. To determine the degree of deterioration, each sample of the magnetic record support was left for 72 hrs. at 50°C and at a

relative humidity of 98%. With an oscillation magnetometer, the change in the magnetic flux density of the sample was determined by the formula

$$\frac{Br' - Br}{Br} \times 100$$

where Br is the initial magnetic flux density and Br' is the density after the test.

The results of the comparative experiments are summarized in the table below, where the values refer to 1.00 as the value for the untreated tapes.

	Change in magnetic flux density
Tape from Example 1	0.25
Untreated tape with vacuum-metallized layer	1.00
Tape as in Example 2	0.38
Untreated tape with layer of ferromagnetic alloy powder	1.00
Tape from Example 3	0.56
Untreated tape with layer precipitated by cathode sputtering	1.00

The table clearly shows the excellent durability and corrosion resistance of the magnetic record support under the invention.

Example 4

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A magnetic layer as in Example 1 was vapor metallized onto a polypyromellithimide-base film marketed by DuPont (E.I.) de Nemours & Co. under the trade name "Kapton." The magnetic layer was coated with a triethoxyvinylsilane solution; heat polymerization was performed for 2 hours at 150°C.

Example 5

A "Kapton" support film 14 μm thick was coated with metal in the same way as in Example 2. A triethoxyvinyl silane solution was applied to the obtained magnetic tape and then heat-polymerized for 2 hrs. at 150°C.

Example 6

A "Kapton" support film 10 μm thick was coated with a magnetic film by cathode sputtering, as explained in Example 3. A triethoxyvinyl silane solution was applied to the magnetic layer and heat-polymerized for 2 hrs. at 150°C.

In the case of Examples 4, 5 and 6, the concentrations of the triethoxyvinyl silane solution were adjusted so that the resulting thin films had the same thicknesses as those in Examples 1, 2 and 3, respectively.

	μ_k	Standstill duration (min)	Change in magnetic flux density
Untreated tape	-	-	1.00
Example 4	0.30	3	0.90
Example 5	0.25	20	0.95
Example 6	0.30	8	1.00

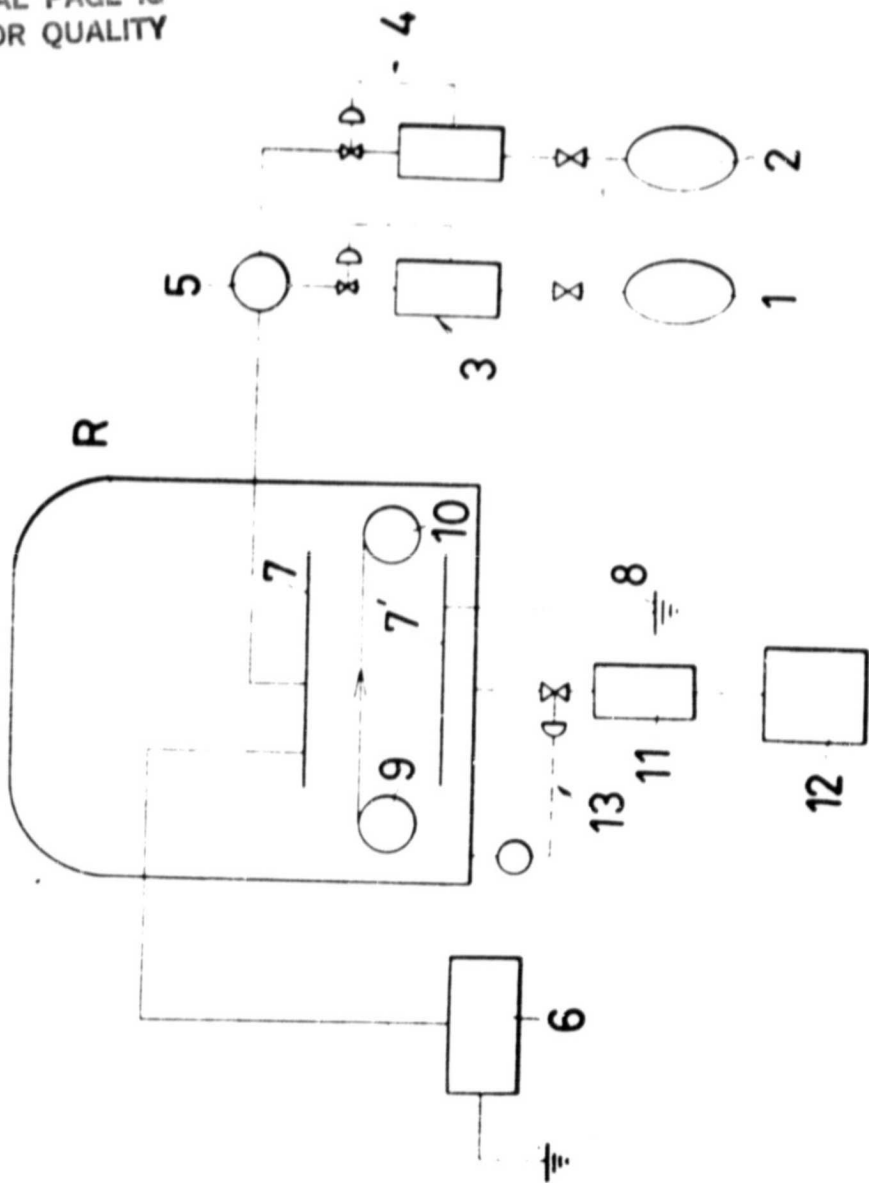
The thin films in Examples 4, 5 and 6 were all hardened during polymerization; nevertheless they did not prove to be as effective as films formed by plasma polymerization. This is attributable to the fact that the plasma polymerization makes the reaction gas sufficiently permeable to form films free of tiny openings, while heat polymerization produces a lower-quality film. A further factor contributing to the marked difference might be that the plasma-polymerized film adheres so firmly to its support that the two form a three-dimensional

structure . Moreover, analyses with the Fourier transform infrared spectrophotometer (ESCA) showed that with heat polymerization, the ethoxy groups remained in the polymer, while plasma polymerization made it possible for the siloxane bond to be present in the product. Examples 4, 5 and 6 show that the monomer presenting the double bonds is usable for heat polymerization, but that the resulting protective film is greatly inferior in its properties to the plasma-polymerized films. Monomers without a double bond are difficult to polymerize with techniques other than plasma polymerization.

Thus the present invention satisfies the strict requirements set for the quality and durability of magnetic record supports. /20

FIG. 1

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16 Juni 1983
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FIG. 2

